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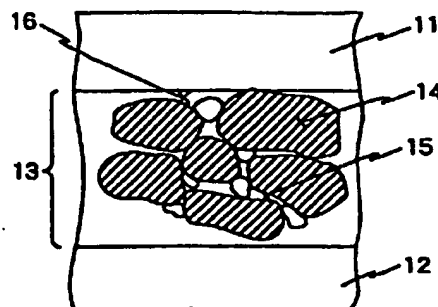
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(54) DIELECTRIC ELEMENT AND MANUFACTURING METHOD THEREFOR

(57) An object is to provide a ferroelectric element having a high P_r and a low E_c and having a good withstand voltage, which is in the form of a thin film using a ferroelectric layer containing insulating particles. The ferroelectric layer containing the insulating particles is effective to suppress leak current caused through grain boundaries of crystals, and hence to exhibit a high P_r and a low E_c and a good withstand voltage. The ferroelectric element has a structure in which such a ferroelectric layer in the form of a thin film is sandwiched between electrodes. By incorporating the ferroelectric element in a field effect transistor structure, it is possible to realize a highly integrated semiconductor device for detecting reading or writing.

FIG. 1



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Description

DISCLOSURE OF INVENTION

TECHNICAL FIELD

[0001] The present invention relates to a ferroelectric element such as an FeRAM utilizing a non-volatile property of a ferroelectric material, a semiconductor device using the ferroelectric element, and a method of manufacturing the ferroelectric element. The present invention also relates to a high dielectric element such as a DRAM utilizing a high dielectric constant and a low leak current density, a semiconductor device using the high dielectric element, and a method of manufacturing the high dielectric element.

BACKGROUND ART

[0002] As a semiconductor memory, there is known a DRAM (Dynamic Random Access Memory) having a feature in terms of rewriting data at a high speed. DRAMs enter in the age of a large capacity of 16 M bits to 64 M bits along with progress of technologies for realizing higher density and higher integration. This also requires a technology for achieving finer-geometries of circuit components, particularly, finer-geometries of capacitors for storing information. For achieving finer-geometries of capacitors, it is required to make thin a dielectric film, to select a material having a high dielectric constant, and to change the structure of the capacitor composed of an upper and a lower electrodes and a dielectric material from two-dimensional to three-dimensional. With respect to a high dielectric material, it is known that BST (Ba/Sr)TiO₃ having a simple lattice perovskite crystal structure exhibits a dielectric constant (ϵ) larger than that of SiO₂/Si₃N₄. An example using such a high dielectric material has been reported in International Electron Device Meeting Technical Digest (IEDM Tech. Dig.), p. 823, 1991.

[0003] A non-volatile memory FeRAM (Ferroelectric Random Access Memory) using a ferroelectric material as a capacitor material has a characteristic capable of storing data in the OFF state of a power supply because it utilizes two residual polarization states being different in polarity. The FeRAM has a feature in terms of rewriting data at a speed being as very high as the order of μ s or less, and therefore, it is expected as an ideal memory in the next generation. In the case of such a FeRAM, it is also required to make thin a ferroelectric film for achieving a large capacity. Incidentally, a semiconductor memory intended to suppress reactivity between a ferroelectric material and a metal electrode has been disclosed in Japanese Patent Application Laid-open No. 5-190797, in which PZT (lead zirconate titanate) is used as a ferroelectric material and a silicon nitride (SiNx) film as a diffusion preventive layer is formed around the ferroelectric material.

[0004] The above-described prior art technologies, however, have failed to examine suppression of a leak current density accompanied by thinning of a dielectric material essentially to be performed for increasing the degree of integration. A memory using the above-described BST is aimed at lowering an operational voltage along with higher integration. For lowering an operational voltage for a memory, it is required to ensure a sufficient capacitance at a small voltage. To increase such a capacitance, it has been examined to select a material having a high dielectric constant, to increase an electrode area, and to make thin a high dielectric material. A thin film made of BST having a polycrystalline structure, however, has a problem in terms of withstand voltage characteristic because such a polycrystalline film allows leak current to easily flow through grain boundaries of crystals. For this reason, in the case of using the BST thin film as a capacitor, it was difficult to apply a sufficient operational voltage thereto.

[0005] In the above ferroelectric capacitor in which the silicon nitride film is formed around the PZT film, the silicon nitride film acts as a diffusion preventive layer capable of preventing thermal diffusion from elements of PZT thereby keeping a desirable stoichiometric composition of the ferroelectric material necessary for ferroelectric characteristics. The silicon nitride layer in the abovedescribed prior art ferroelectric capacitor, however, has a problem. Since the silicon nitride film has a dielectric constant being as small as 7, it must be formed to an ultra-thin thickness of 30 Å or less for suppressing lowering the total capacitance of the ferroelectric capacitor having a size of 4 μ m². Further, in the case of higher integration of 1 G bits, the area of the capacitor becomes as small as 0.1 μ m². In this case, it becomes apparent on the basis of simple calculation that the silicon nitride layer must be formed to a further ultra-thin thickness of 1 Å or less.

[0006] Additionally, in the thinning process made in the prior art technologies, if a metal is as an electrode, there occurs a problem that a transition layer is formed by diffusion of an element at an interface between a dielectric thin film and the metal electrode, to thereby reduce a spontaneous polarization (Pr), to increase a field reversing (Ec), and to give rise to a film fatigue.

[0007] To solve the above-described problems, the present invention has been made, and an object of the present invention is to provide a high dielectric layer containing insulating particles, which is capable of suppressing leak current caused through grain boundaries of crystals and which can be thinned to such an extent as to meet a requirement of high integration; a high dielectric element in which the high dielectric thin film is sandwiched between upper and lower electrodes; a semiconductor device using the high dielectric element; and a method of manufacturing the high dielectric element.

[0008] Another object of the present invention is to solve the above-described problems and to provide a ferroelectric layer containing insulating particles, which is capable of suppressing leak current caused through grain boundaries of crystals and which can be thinned to such an extent as to meet a requirement of high integration; a ferroelectric element in which the ferroelectric thin film is sandwiched between upper and lower electrodes; a semiconductor device using the ferroelectric element; and a method of manufacturing the ferroelectric element.

[0009] A further object of the present invention is to provide a high dielectric element or a ferroelectric element including the above high dielectric thin film or the above ferroelectric thin film having a thickness of 200 Å or more, wherein the element is allowed to be applied with an operation voltage of 2 V for operating a semiconductor memory.

[0010] A further object of the present invention is to provide a high dielectric element in which a conductive oxide is used as an electrode being in contact with the above high dielectric thin film to suppress formation of a transition layer, and a method of manufacturing the high dielectric element.

[0011] A further object of the present invention is to provide a ferroelectric element in which a conductive oxide is used as an electrode being in contact with the above ferroelectric thin film to suppress formation of a transition layer, and a method of manufacturing the ferroelectric element.

[0012] To achieve the above objects, according to the present invention, there is provided a ferroelectric element including an upper electrode, a ferroelectric thin film, and a lower electrode, wherein the ferroelectric layer contains insulating particles having a resistance of $10^6 \Omega$ or more.

[0013] According to the present invention, there is provided a high dielectric element including an upper electrode, a high dielectric thin film, and a lower electrode, wherein the high dielectric layer contains insulating particles having a resistance of $10^6 \Omega$ or more.

[0014] The insulating particles have particle sizes each being in a range of 50 Å or less.

[0015] The ferroelectric thin film may be made of one kind selected from the group consisting of a material expressed by $(\text{Pb}_{1-x}\text{A}_x)(\text{Zr}_{1-y}\text{Ti}_y)\text{O}_3$ (where A is one kind selected from the group consisting of La, Ba, and Nb), and a material expressed by $(\text{AO})^{2+}(\text{B}_{y-1}\text{C}_y\text{O}_{3y+1})^{2-}$ (where A is at least one kind selected from the group consisting of Ti, Hg, Pb, Bi, and a rare earth element; B is at least one kind selected from the group consisting of Bi, Pb, Ca, Sr, and Ba; C is at least one kind selected from the group consisting of Ti, Nb, Ta, W, Mo, Fe, Co, Cr and Zr; and $y = 2, 3, 4$, and 5).

[0016] The high dielectric thin film may be made of one kind selected from the group consisting of a material expressed by $(\text{Ba}_{1-x}\text{Sr}_x)\text{TiO}_3$ and a material expressed by $(\text{Pb}_{1-x}\text{A}_x)(\text{Zr}_{1-y}\text{Ti}_y)\text{O}_3$ (where A is one kind

selected from the group consisting of La, Ba and Nb).

[0017] The insulating particles may be those of a compound containing Si.

[0018] The lower electrode may be composed of a metal, a conductive oxide of a single element, and a conductive oxide having a perovskite structure which are formed on a base substrate in this order, and each of the conductive oxides may be oriented along a specific plane.

[0019] The upper electrode may be composed of a conductive oxide having a perovskite structure and a metal or comprises a conductive oxide having a perovskite structure, a conductor oxide of a single element, and a metal, which are formed in this order from the side in contact with the ferroelectric thin film or the high dielectric thin film.

[0020] In the case where the ferroelectric thin film has a thickness of 200 Å or more, the ferroelectric element may exhibit a withstand voltage of 2 V or more at a leak current density of 10^{-5} A/cm^2 or less.

[0021] In the case where the high dielectric thin film has a thickness of 200 Å or more, the high dielectric element may exhibit a withstand voltage of 2 V or more at a leak current density of 10^{-5} A/cm^2 or less.

[0022] The metal used for the electrode may be at least one kind selected from the group consisting of Pt, Au, Al, Ni, Cr, Ti, Mo, and W. Also, to realize the function of the electrode material, a conductive oxide of a single element or a perovskite structure, which has a resistivity of $1 \text{ m}\Omega \cdot \text{cm}$ or less, may be used as the electrode. The conductive oxide of a single element may be an oxide of at least one kind selected from the group consisting of Ti, V, Eu, Cr, Mo, W, Ph, Os, Ir, Pt, Re, Ru and Sn. The conductive oxide having a perovskite structure may be at least one kind of perovskite oxide selected from the group consisting of ReO_3 , SrReO_3 , BaReO_3 , LaTiO_3 , SrVO_3 , CaCrO_3 , SrCrO_3 , SrFeO_3 , $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ ($0 < x < 0.5$), LaNiO_3 , CaRuO_3 , SrRuO_3 , SrTiO_3 , and BaPbO_3 , and has a resistivity of $1 \text{ m}\Omega \cdot \text{cm}$ or less.

[0023] According to the present invention, there is provided a method of forming the ferroelectric thin film, including the step of forming the ferroelectric thin film by sputtering in an atmosphere of a mixed gas of oxygen and an inert gas at a temperature of 650°C or less. In addition, the film formation temperature is selected to suppress reaction with an electrode. Instead of the sputtering method described above, the ferroelectric thin film may be formed by MOCVD in an atmosphere of oxygen or excited oxygen at a temperature of 650°C or less.

[0024] According to the present invention, there is provided a method of forming the ferroelectric thin film, including the step of forming the ferroelectric thin film by applying a starting material composed of a metal alkoxide or a metal salt of an organic acid on a substrate by spin-coating or dip-coating and baking the film at a normal pressure and at a temperature of 650°C or less. In

addition, the film formation temperature is selected to suppress a reaction with the electrode.

[0025] According to the present invention, there is provided a method of forming the high dielectric thin film, including the step of forming the high dielectric thin film by sputtering in an atmosphere of a mixed gas of oxygen and an inert gas at a temperature of 650°C or less. In addition, the film formation temperature is selected to suppress reaction with the electrode. Instead of the sputtering method described above, the high dielectric thin film may be formed by MOCVD in an atmosphere of oxygen or excited oxygen at a temperature of 650°C or less.

[0026] According to the present invention, there is provided a method of forming the high dielectric thin film, including the step of forming the high dielectric thin film by applying a starting material composed of a metal alkoxide or a metal salt of an organic acid on a substrate by spin-coating or dip-coating and baking the film at a normal pressure and at a temperature of 650°C or less. In addition, the film formation temperature is selected to suppress a reaction with the electrode. According to the present invention, there is provided a method of forming the conductive oxide of a single element or a perovskite structure, including the step of forming a conductive oxide of a single element or a perovskite structure by sputtering in an atmosphere of a mixed gas of oxygen and an inert gas at a temperature of 650°C or less. Instead of the sputtering method described above, the conductive oxide of a single element or the perovskite structure may be formed by MOCVD in an atmosphere of oxygen or excited oxygen at a temperature of 650°C or less.

[0027] According to the present invention, there is provided a method of forming the conductive oxide of a single element or the provskite structure, including the step of forming the conductive oxide of a single element or the provskite structure by applying a starting material composed of a metal alkoxide or a metal salt of an organic acid on a substrate by spin-coating or dip-coating and baking the film at a normal pressure and at a temperature of 650°C or less. In addition, the film formation temperature is selected to suppress a reaction with an electrode.

[0028] Further, in the step of forming the ferroelectric thin film from a starting material composed of a metal alkoxide or a metal salt of an organic acid by spin-coating or dip-coating, the ferroelectric thin film may be formed while irradiating ultraviolet rays to the ferroelectric thin film. This is based on the knowledge that the decomposition of a raw material caused by light irradiation is considered effective for lowering the film formation temperature. The high dielectric thin film may be also formed while irradiating ultraviolet rays to the high dielectric thin film in the same manner as described above, and further, the conductive oxide may be formed while irradiating ultraviolet rays to the high dielectric thin film in the same manner as described above

[0029] According to the present invention, there is provided a semiconductor device, wherein the structure including the upper electrode, the ferroelectric thin film, and the lower electrode is formed as a capacitor in a structure of a field effect transistor.

[0030] Further, according to the present invention, there is provided a semiconductor device, wherein the structure including the upper electrode, the high dielectric thin film, and the lower electrode is formed as a capacitor in a structure of a field effect transistor.

BRIEF DESCRIPTION OF DRAWINGS

[0031]

Fig. 1 is a schematic view of a ferroelectric layer of the present invention;

Fig. 2 is a schematic view of a prior art ferroelectric layer;

Fig. 3 is a sectional view showing a ferroelectric element of the present invention;

Fig. 4 is a sectional view showing a high dielectric element of the present invention;

Fig. 5 is a photograph by a TEM, showing the ferroelectric layer of the present invention;

Fig. 6 is a graph showing data on a leak current density of the ferroelectric element of the present invention;

Fig. 7 is a sectional view showing an internal configuration of a lower electrode of the present invention;

Fig. 8 is a sectional view showing an internal configuration of a lower electrode of the present invention;

Fig. 9 is a sectional view showing a semiconductor device using the ferroelectric element of the present invention; and

Fig. 10 is a graph showing a relationship between a film thickness and a withstand voltage characteristic for the ferroelectric element of the present invention.

BEST MODE FOR CARRYING OUT THE INVENTION

[0032] Hereinafter, embodiments of the present invention will be described with reference to the drawings. The present invention, however, is not limited thereto.

[0033] In addition, reference numerals in the drawings are as follows:

[0034] Each of reference numerals 31, 41, 81, 91 indicates an upper electrode; each of 32, 71, 81, and 92 is a ferroelectric thin film; 42 is a high dielectric thin film; each of 33, 43, 83, and 93 is a lower electrode; each of 34, 44, and 75 is a base substrate; each of 72 and 82 is a conductive oxide having a perovskite structure; each of 73 and 83 is a conductive oxide of a single element; each of 74 and 84 is a metal; each of 94 and 96 is a SiO₂ film; 95 is Si; 97 is a diffusion layer; 98 is a gate electrode; and 99 is a SiO₂ gate film.

(Embodiment 1)

[0035] Fig. 1 is a view showing a structure including an upper electrode 11, a ferroelectric layer 13, and a lower electrode 12 according to the present invention. In the ferroelectric layer 13, insulating particles 16 containing Si are precipitated at crystal grain boundaries 15 between crystals 14 of a ferroelectric material. Such a structure makes it possible to suppress reduction in withstand voltage characteristic which is, as shown by a comparative example of Fig. 2, due to a leak current 21 flowing through grain boundaries of crystals of a ferroelectric material, and hence to apply an operational voltage essential for operation of a memory. Further, since particle sizes of the insulating particles are each in a range of 50 Å or less, the insulating particles exert only a small effect on the capacitance of a capacitor even if the insulating particles have a dielectric constant smaller than that of the dielectric material. As a result, the capacitor having such a structure can satisfy a capacitance being more than 30 fF necessary for a DRAM.

[0036] Next, there will be described a method of preparing a ferroelectric thin film made from a material expressed by a chemical structural formula of $(AO)^{2+}(B_1C_2O_7)^{2-}$ where A = Bi, B = Sr, and C = Ta. In a sectional view of a ferroelectric element shown in Fig. 3, reference numeral 34 indicates a base substrate. First, as the base substrate 34, there was used a Si wafer on which a TiN layer as a barrier layer was formed to a thickness of 200 Å at a temperature of 300°C and a SiO₂ layer was formed thereon by thermal oxidation. Then, a base electrode 33 was formed on the base substrate 34. As the backing electrode, a Pt thin film was formed to a thickness of 1,000 Å by sputtering at a temperature of 350°C. A ferroelectric thin film 32 was then formed on the lower electrode 33 as follows. First, a solution of alkoxides of Bi, Sr, Ta, and Si was applied on the lower electrode 33 by spin-coating at 1,500 rpm for 30 sec, being dried at 150°C for 5 min, and then subjected to pre-heat treatment in air or oxygen at a temperature of 200 to 550°C lower than a crystallization temperature of the ferroelectric thin film, that is, 580°C for 10 to 30 min. Such a procedure was taken as one cycle, and the cycle was repeated 2-5 times, to form a precursor thin film having a thickness of 1,000 Å. The precursor thin film was finally heat-treated at a temperature of 580 to 650°C, to obtain a ferroelectric layer of $(Bi_2O_2)^{2+}(SrTa_2O_7)^{2-}$ containing an amorphous Si compound.

[0037] The ferroelectric layer thus obtained was observed by a TEM, which gave a result shown in Fig. 5. As is apparent from Fig. 5, amorphous particles having particle sizes each in a range of 20 to 50 Å were recognized between crystals of the ferroelectric material having particle sizes each in a range of 100 to 1,000 Å. The amorphous particles were those of a compound containing Si, Bi, Sr and Ta. The composition of the

compound was largely dependent on the state of the particles.

[0038] A result of examining a relationship between a voltage and a leak current density for such a ferroelectric element is shown in Fig. 6. For the prior art ferroelectric element containing no particles, a leak current density was as large as 10^{-4} A/cm² at 1 V. As a result, the prior art ferroelectric element could not be used as a capacitor. On the contrary, for the ferroelectric element containing particles, the leak current density was as very small as 1×10^{-7} A/cm² or less at 5 V. This shows that the ferroelectric element containing particles exhibits a very good withstand voltage characteristic. The ferroelectric element containing particles also exhibited good ferroelectric characteristics. That is, 2Pr was 16 μC/cm² at 3 V, Ec was 40 kV/cm, and degradation of the characteristics was about 3% after writing 10^{15} times by positive/negative reversal of a voltage of 3 V. Consequently, in the ferroelectric element containing particles, reduction in characteristics due to precipitation of particles was not recognized.

[0039] A relationship between a film thickness and a withstand voltage characteristic for the ferroelectric layer of $(Bi_2O_2)^{2+}(SrTa_2O_7)^{2-}$ containing the above insulating particles is shown in Fig. 10. Samples each having a film thickness of 200 to 2,000 Å were prepared by changing the above-described cycle of the procedure for forming a precursor thin film. As is apparent from Fig. 10, the withstand voltage was 2 V or more at the leak current density of 10^{-5} A/cm² for the samples each having a film thickness of 200 Å or more.

[0040] Although in the above embodiment description is made using $(Bi_2O_2)^{2+}(SrTa_2O_7)^{2-}$ as the ferroelectric material, a solution of an alkoxide of Si may be added to a ferroelectric material having a perovskite crystal structure expressed by a chemical structural formula of $(AO)^{2+}(B_{y-1}CyO_{3y+1})^{2-}$ where the A site is at least one kind selected from the group consisting of Ti, Hg, Y, Ce, Pr, Nd, Pm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu; the B site is at least one kind or more selected from the group consisting of Bi, Pb, Ca, Sr, and Ba; the C site is at least one kind or more selected from the group consisting of Ti, Nb, Ta, W, Mo, Fe, Co, Cr, and Zr; and y = 2, 3, 4, and 5.

[0041] Further, another ferroelectric thin film 32 was formed on the lower electrode 33 obtained in the same manner as described above, as follows. First, a solution of alkoxides of Pb, Zr, Ti, and Si was applied on the lower electrode 33 by spin-coating at 1,500 rpm for 30 sec, being dried at 150°C for 5 min, and then subjected to pre-heat treatment in air or oxygen at a temperature of 200 to 400°C lower than a crystallization temperature of the ferroelectric thin film, that is, 450°C for 10 to 30 min. Such a procedure was taken as one cycle, and the cycle was repeated 2-5 times, to form a precursor thin film having a thickness of 1,000 Å. The precursor thin film was finally heat-treated at a temperature of 500 to 650°C, to obtain a ferroelectric layer of $Pb(Zr_{0.5}Ti_{0.5})O_3$.

containing an amorphous Si compound. For this ferroelectric element containing particles, the leak current density was as very small as 1×10^{-7} A/cm² or less at 5 V. This shows that the ferroelectric element exhibits a very good withstand voltage characteristic. The ferroelectric element also exhibited good ferroelectric characteristics. For example, 2Pr was 40 μ C/cm² at 3 V, Ec was 60 kV/cm, and degradation of characteristics was about 3% after writing 1012 times by \pm reversal of a voltage of 3 V. Consequently, reduction in characteristics due to precipitation of particles was not recognized. Further, with respect to the dependency of the film thickness on the withstand voltage, the withstand voltage was 2 V or more at the leak current density of 10^{-5} A/cm² for the samples each having a thickness of 200 Å or more.

[0042] Although in the above embodiment description is made using $\text{Pb}(\text{Zr}_{0.5}\text{Ti}_{0.5})\text{O}_3$ as the ferroelectric material, a solution of an alkoxide of Si may be added to a ferroelectric material having a perovskite crystal structure expressed by a chemical structural formula of $(\text{Pb}_{1-x}\text{A}_x)(\text{Zr}_{1-y}\text{Ti}_y)\text{O}_3$ where the A site is substituted for at least one kind or more selected from a group consisting of La, Ba, and Nb; and each of x and y is in a range of 0 to 1.

(Embodiment 2)

[0043] Next, there will be described a method of preparing a high dielectric layer having a crystal structure expressed by $(\text{Ba}_{0.5}\text{Sr}_{0.5})\text{TiO}_3$ used in this embodiment. In a sectional view of a high dielectric element shown in Fig. 4, reference numeral 44 indicates a base substrate. As the base substrate, there was used a Si wafer on which a TiN layer as a barrier layer was formed to a thickness of 200 Å at a temperature of 300°C and a SiO_2 layer was then formed by thermal oxidation. Then, a lower electrode 43 was formed on the base substrate 44. As the lower electrode, a Pt thin film having a thickness of 1,000 Å by sputtering at a temperature of 350°C. A high dielectric thin film 42 was formed on the lower electrode 43 as follows. First, a solution of alkoxides of Ba, Sr, Ti, and Si was applied on the lower electrode 43 by spin-coating at 1,500 rpm for 30 sec, being dried at 150°C for 5 min, and then subjected to pre-heat treatment in air or oxygen at a temperature of 200 to 550°C lower than a crystallization temperature of the ferroelectric thin film, that is, 580°C for 10 to 30 min. Such a procedure was taken as one cycle, and the cycle was repeated 2-5 times, to form a precursor thin film having a thickness of 1,000 Å. The precursor thin film was finally heat-treated at a temperature of 580 to 650°C, to thus obtain a high dielectric layer of $(\text{Ba}_{0.5}\text{Sr}_{0.5})\text{TiO}_3$ containing an amorphous Si compound. The high dielectric layer thus obtained was observed by a TEM, which gave a result in which amorphous particles having particle sizes each in a range of 20 to 50 Å were recognized between crystals of the high

dielectric material having particle sizes each in a range of 100 to 500 Å. The particles were those of a compound containing Si, Ba, Sr and Ti, and the composition of the compound was largely dependent on the state of particle. As a result of examining a relationship between a voltage and a leak current density for the high dielectric element, it was found that the leak current density was as very small as 1×10^{-7} A/cm² or less at 3 V. This shows that the ferroelectric element containing particles exhibits a very good withstand voltage characteristic. The ferroelectric element also exhibited a dielectric constant (ϵ) of 250 at a frequency of 1 MHz which was larger than that of SiN_x , and consequently, it was found that degradation of characteristics due to precipitation of particles was not recognized. With respect to the dependency of the film thickness on the withstand voltage, the withstand voltage was 2 V or more at the leak current density of 10^{-5} A/cm² for the high dielectric thin film having a thickness of 200 Å or more.

[0044] Although in the above embodiment description is made using $(\text{Ba}_{0.5}\text{Sr}_{0.5})\text{TiO}_3$ as the ferroelectric material, a solution of an alkoxide of Si may be added to a high dielectric material having a perovskite crystal structure expressed by a chemical formula of $(\text{Ba}_{1-x}\text{Sr}_x)\text{TiO}_3$ where x is adjusted in a range of 0 to 1.

(Embodiment 3)

[0045] Fig. 7 is a view showing an internal configuration of a lower electrode in this embodiment. The lower electrode includes a metal 74, a conductive oxide 73 of a single element, and a conductive oxide 72 having a perovskite structure. Although in each of the embodiments 1 and 2, description is made using a metal electrode as the lower electrode, a lower electrode in contact with a ferroelectric material is made from a conductive oxide having a perovskite structure in this embodiment. Such a lower electrode was effective to suppress an oxygen loss layer having been generally recognized at an interface between a ferroelectric material and a metal electrode, and hence to suppress lowering of Pr due to reversal of voltage. In formation of this lower electrode, the metal, conductive oxide of a single element, and conductive oxide having a perovskite structure were laminated in this order on a base substrate. This was effective to improve adhesiveness between adjacent ones of the layers. This was also effective to control orientation of the conductive oxide having a perovskite structure and hence to form a ferroelectric thin film or a high dielectric thin film on the conductive oxide while controlling orientation of the thin film. Hereinafter, there will be described a method of preparing the lower electrode. First, the metal 74 represented by Ru was formed on the above-described base substrate 34 to a thickness of 1,000 Å by sputtering at a temperature of 600°C; the conductive oxide 73 of a single element represented by RuO was formed thereon to a thickness of 1,000 Å by sputtering in an oxygen

atmosphere at a temperature of 450°C; and the conductive oxide 72 having a perovskite structure represented by SrRuO_3 , was formed thereon to a thickness of 1,000 Å by sputtering at a temperature of 650°C. On the lower electrode 33 was formed a ferroelectric layer of $(\text{Bi}_2\text{O}_3)^{2+}(\text{SrTa}_2\text{O}_7)^{2-}$ containing an amorphous Si compound in the same manner as in the first embodiment. The orientation of the ferroelectric thin film was examined by X-ray diffraction, which gave the result in which the C-axis was tilted 45°. Further, the pole figure measurement using a diffraction peak of the (105) face showed that the degree of orientation was 93%.

[0046] Next, a configuration of an upper electrode in this embodiment is shown in Fig. 8(a). An upper electrode 31 includes a conductive oxide 82 having a perovskite structure, a conductive oxide 83 of a single element, and a metal 84. Like the case of using the conductive oxide as the lower electrode, the above upper electrode 31 was effective to suppress an oxygen loss layer having been generally recognized at an interface between a ferroelectric material and a metal electrode. A conductive oxide having a perovskite structure, represented by SrRuO_3 , was formed on the above ferroelectric layer of $(\text{Bi}_2\text{O}_3)^{2+}(\text{SrTa}_2\text{O}_7)^{2-}$ containing an amorphous Si compound to a thickness of 1,000 Å by sputtering in an oxygen atmosphere at a temperature of 650°C. Further, the conductive oxide 83 of a single element, represented by RuO_3 , was formed thereon to a thickness of 1,000 Å by sputtering in an oxygen atmosphere at a temperature of 450°C, and then the metal 84 represented by Ru was formed thereon to a thickness of 1,000 Å by sputtering at a temperature of 600°C. The ferroelectric element exhibited good ferroelectric characteristics. For example, the leak current density was $1 \times 10^{-8} \text{ A/cm}^2$ at 5 V; 2Pr was $16 \text{ } \mu\text{C/cm}^2$ at 3 V and E_c was 40 kV/cm; and degradation of characteristic was about 5% after rewriting 10^{15} times by positive/negative reversal of a voltage of 3 V.

[0047] Although in this embodiment description is made using $(\text{Bi}_2\text{O}_3)^{2+}(\text{SrTa}_2\text{O}_7)^{2-}$ as the ferroelectric material, there may be used the ferroelectric material expressed by the chemical structural formula of $(\text{AO})^{2+}(\text{B}_{1-x}\text{C}_x\text{O}_{3y+1})^{2-}$ or the ferroelectric material expressed by the chemical structural formula of $(\text{Pb}_{1-x}\text{A}_x)(\text{Zr}_{1-y}\text{Ti}_y)\text{O}_3$ in the first embodiment, or the high dielectric material expressed by the chemical structural formula of $(\text{Ba}_{1-x}\text{Sr}_x)\text{TiO}_3$ in the second embodiment.

[0048] With respect to the above upper and lower electrodes, specific examples of the metal may include Pt, Au, Al, Ni, Cr, Ti, Mo, and W; specific examples of the conductive oxide of a single element may include TiO_x , VO_x , EuO , CrO_2 , MoO_2 , WO_2 , PhO , OsO , IrO , PtO , ReO_2 , RuO_2 , and SnO_2 ; and specific examples of the conductive oxide having a perovskite structure may include ReO_3 , SrReO_3 , BaReO_3 , LaTiO_3 , SrVO_3 , CaCrO_3 , SrCrO_3 , SrFeO_3 , $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ ($0 < x < 0.5$), LaNiO_3 , CaRuO_3 , SrRuO_3 , SrTiO_3 , and BaPbO_3 .

[0049] Further, after formation of the lower elec-

trode, and a ferroelectric thin film or a high dielectric thin film in the same manner as described above, another upper electrode of the present invention shown in Fig. 8(b) was formed, as follows. Like the above embodiment, a conductive oxide 82 having a perovskite structure, represented by either of ReO_3 , SrReO_3 , BaReO_3 , LaTiO_3 , SrVO_3 , CaCrO_3 , SrCrO_3 , SrFeO_3 , $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ ($0 < x < 0.5$), LaNiO_3 , CaRuO_3 , SrRuO_3 , SrTiO_3 , and BaPbO_3 was formed to a thickness of 1,000 Å by sputtering in an oxygen atmosphere at a temperature of 650°C, and then a metal 84, represented by either of Pt, Au, Al, Ni, Cr, Ti, Mo, and W was formed to a thickness of 1,000 Å by sputtering at a temperature of 600°C, to form an upper electrode, thereby preparing a ferroelectric element or a high dielectric element.

(Embodiment 4)

[0050] Although a metal alkoxide is used as a starting material for spin-coating for forming a high dielectric thin film in each of Embodiments 1 to 3, a ferroelectric thin film or a high dielectric thin film can be prepared by spin-coating using as a starting material a metal acetylacetonate, a metal carbonate, an acetate, or a metal soap such as a metal naphthenate or metal octylate.

[0051] Similarly, a ferroelectric thin film or a high dielectric thin film can be prepared in the same process as described above by dip-coating using as starting material a metal alkoxide, a metal acetylacetonate, a metal carbonate, an acetate, or a metal soap such as a metal naphthenate or metal octylate.

[0052] In preparation of a ferroelectric thin film or a high dielectric thin film in each of Embodiments 1 to 3, a ferroelectric thin film or a high dielectric thin film having a thickness of 1,000 Å was obtained by sputtering in an atmosphere containing oxygen gas at a pressure of 0.02 to 10^{-4} torr at a temperature of 530 to 650°C for 1 hr.

[0053] Also, in preparation of a ferroelectric thin film or a high dielectric thin film in each of Embodiments 1 to 3, a ferroelectric thin film or a high dielectric thin film having a thickness of 1,000 Å was obtained by laser vapor-deposition using a sintered body having the same composition as that of the above high dielectric thin film in an atmosphere containing oxygen gas at a pressure of 0.3 to 10^{-4} torr at a temperature of 530 to 650°C for 1 hr.

[0054] Further, in preparation of a ferroelectric thin film or a high dielectric thin film in each of Embodiments 1 to 3, a ferroelectric thin film or a high dielectric thin film having a thickness of 1,000 Å was obtained by MOCVD using β -diketone complex compound, or phenyl-group or o-tolyl group compound as a starting material in an atmosphere containing oxygen gas at a pressure of 0.3 to 10^{-4} torr at a temperature of 530 to 650°C for 2 hr.

[0055] In the above laser vapor-deposition or MOCVD process, a ferroelectric thin film or a high dielectric film having a thickness of 1,000 Å was obtained

in an atmosphere containing excited oxygen (ozone, ECR or microwave plasma) at a pressure of 0.3 to 10^{-4} torr at a temperature of 500 to 620°C for 1 - 2 hr.

[0056] Further, in preparation of either of a metal, a conductive oxide of a single element, a conductive oxide of a perovskite structure in each embodiment, by carrying out the same process as described above, it is possible to a metal, a conductive oxide of a single element, a conductive oxide of a perovskite structure like the above examples in this embodiment.

(Embodiment 5)

[0057] Fig. 9 is a view showing a semiconductor device including a ferroelectric element. The semiconductor device is prepared in the following manner. First, a diffusion layer 97 is formed on an Si wafer 95 by ion implantation and heat-treatment; an SiO_2 gate film 99 is formed thereon by surface oxidation; and a gate electrode 98 is formed thereon. After formation of an SiO_2 film 94 and an SiO_2 film 96 for element isolation between a transistor and a capacitor, an aluminum interconnection 910 is formed to connect an upper electrode 91 to the diffusion layer 97. As a ferroelectric element, a structure including the upper electrode 91, a ferroelectric thin film 92 and a lower electrode 93, which was prepared in Embodiments 1 to 4, was formed to obtain a semiconductor device including the ferroelectric element. The semiconductor device including the ferroelectric element thus obtained enables detection by a change in stored charge capacitance obtained at a voltage of 3 V.

[0058] Although in this embodiment description is made using the structure including the upper electrode 91, ferroelectric thin film 92, and lower electrode 93, there may be formed a high dielectric element having a structure including an upper electrode, a high dielectric thin film, and a lower electrode. The semiconductor device including the high dielectric element thus obtained has a storage charge capacitance of 30 fF at a voltage of 3 V.

FIELD OF INDUSTRIAL APPLICATION

[0059] As described above, according to the present invention, there can be provided a highly integrated ferroelectric element having a high P_r and a low E_c and having a good withstand voltage, in which a ferroelectric layer thinned to a thickness of 200 Å or more is sandwiched between electrode, wherein the ferroelectric layer contains insulating particles to suppress leak current caused through grain boundaries of crystals.

[0060] As described above, according to the present invention, there can be provided a high dielectric element having a high dielectric constant and a good withstand voltage, which is thinned to a thickness of 200 Å or more and includes a high dielectric layer,

wherein the ferroelectric layer contains insulating particles to suppress leak current caused through grain boundaries of crystals.

[0061] A semiconductor device including a ferroelectric element can be formed by incorporating the above ferroelectric element in a field effect transistor structure.

[0062] Further, a semiconductor device including a high dielectric element can be formed by incorporating the above high dielectric element in a field effect transistor structure.

[0063] As described above, this invention is effective to be applied to a highly integrated ferroelectric element or high dielectric element, and a semiconductor device using the same.

Claims

1. A dielectric element comprising an upper electrode, a dielectric thin film, and a lower electrode, wherein said dielectric thin film contains insulating particles having a resistance not smaller than $10^6 \Omega$.
2. A dielectric element according to claim 1, wherein said dielectric thin film comprises at least one of a ferroelectric thin film and a high dielectric thin film.
3. A dielectric element according to any one of claims 1 and 2, wherein said insulating particles each have a particle size not larger than 50 Å.
4. A dielectric element according to claim 2, wherein said ferroelectric thin film is made of one kind selected from the group consisting of a material expressed by $(\text{Pb}_{1-x}\text{A}_x)(\text{Zr}_{1-y}\text{Ti}_y)\text{O}_3$ (where A is one kind selected from the group consisting of La, Ba, and Nb), and a material expressed by $(\text{AO})^{2+}(\text{B}_{y-1}\text{C}_y\text{O}_{3y+1})^{2-}$ (where A is at least one kind selected from a group consisting of Ti, Hg, Pb, Bi, and rare earth elements; B is at least one kind selected from the group consisting of Bi, Pb, Ca, Sr, and Ba; C is at least one kind selected from the group consisting of Ti, Nb, Ta, W, Mo, Fe, Co, Cr and Zr; and $y = 2, 3, 4$, and 5).
5. A dielectric element according to claim 2, wherein said high dielectric thin film is made of one kind selected from the group consisting of a material expressed by $(\text{Ba}_{1-x}\text{Sr}_x)\text{TiO}_3$ and a material expressed by $(\text{Pb}_{1-x}\text{A}_x)(\text{Zr}_{1-y}\text{Ti}_y)\text{O}_3$ (where A is one kind selected from the group consisting of La, Ba and Nb).
6. A dielectric element according to claim 1, wherein said insulating particles are those of a chemical compound containing Si.
7. A dielectric element according to claim 1, wherein

said lower electrode comprises a metal, a conductive oxide of a single element, and a conductive oxide having a perovskite structure which are formed on a base substrate in this order, and each of said conductive oxides is oriented along a specific plane.

8. A dielectric element according to claim 2, wherein said upper electrode comprises a conductive oxide having a perovskite structure and a metal or comprises a conductive oxide having a perovskite structure, a conductor oxide of a single element, and a metal, which are formed in this order from the side in contact with said ferroelectric thin film or said high dielectric thin film.
9. A dielectric element according to claim 4, wherein said ferroelectric thin film has a thickness of 200 Å or more, and said dielectric element exhibits a withstand voltage not lower than 2 V at a leak current density not larger than 10^{-5} A/cm².
10. A dielectric element according to claim 5, wherein said high dielectric thin film has a thickness of 200 Å or more, and said dielectric element exhibits a withstand voltage not lower than 2 V at a leak current density not larger than 10^{-5} A/cm².
11. A dielectric element according to any one of claims 7 and 8, wherein said metal is at least one kind selected from the group consisting of Pt, Au, Al, Ni, Cr, Ti, Mo, and W.
12. A dielectric element according to any one of claims 7 and 8, wherein said conductive oxide of a single element is an oxide of at least one kind selected from the group consisting of Ti, V, Eu, Cr, Mo, W, Ph, Os, Ir, Pt, Re, Ru and Sn, and has a resistivity not larger than 1 mΩ · cm.
13. A dielectric element according to any one of claims 7 and 8, wherein said conductive oxide having a perovskite structure is at least one kind of perovskite oxide selected from the group consisting of ReO₃, SrReO₃, BaReO₃, LaTiO₃, SrVO₃, CaCrO₃, SrCrO₃, SrFeO₃, La_{1-x}Sr_xCoO₃ (0 < x < 0.5), LaNiO₃, CaRuO₃, SrRuO₃, SrTiO₃, and BaPbO₃, and has a resistivity not larger than 1 mΩ · cm.
14. A method of forming a dielectric thin film, comprising the step of forming the dielectric thin film by sputtering in an atmosphere of a mixed gas of oxygen and an inert gas at a temperature not higher than 650°C.
15. A method of forming a dielectric thin film, comprising the step of forming the dielectric thin film by MOCVD in an atmosphere of oxygen or excited

oxygen at a temperature not higher than 650°C.

16. A method of forming a ferroelectric thin film or a high dielectric thin film, comprising the step of forming the ferroelectric thin film or the high dielectric thin film by applying a starting material composed of a metal alkoxide or a metal salt of an organic acid on a substrate by spin-coating and baking the film at a normal pressure and at a temperature not higher than 650°C.
17. A method of forming a ferroelectric thin film or a high dielectric thin film, comprising the step of forming the ferroelectric thin film or the high dielectric thin film by applying a starting material composed of a metal alkoxide or a metal salt of an organic acid on a substrate by dip-coating and baking the film at a normal pressure and at a temperature not higher than 650°C.
18. A method of forming a ferroelectric thin film or a high dielectric thin film according to any one of claims 16 and 17, wherein in a case of forming the ferroelectric thin film or the high dielectric thin film from a starting material composed of a metal alkoxide or a metal salt of an organic acid by spin-coating or dip-coating, the method comprises the step of forming the ferroelectric thin film or the high dielectric thin film while irradiating ultraviolet rays to the ferroelectric thin film or the high dielectric thin film.
19. A semiconductor device, wherein said dielectric element according to claim 1 is formed as a capacitor in a structure of a field-effect transistor.

FIG. 1

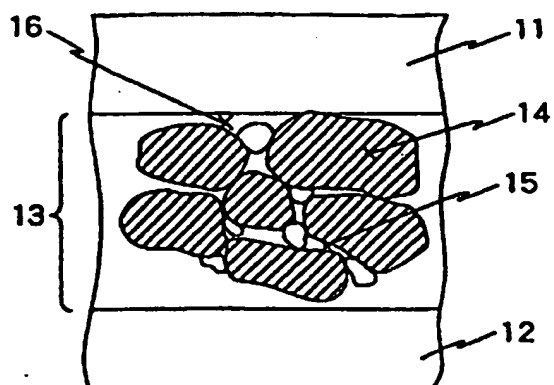


FIG. 2

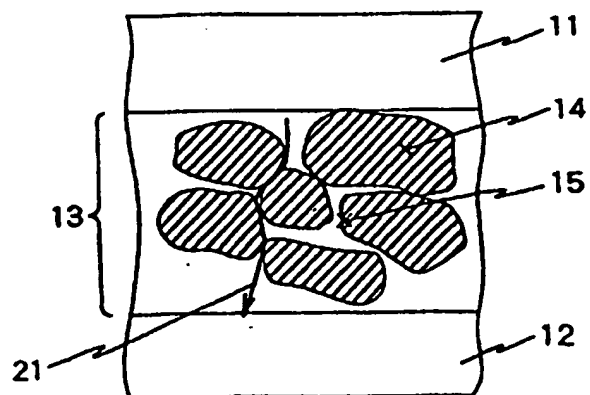


FIG. 3

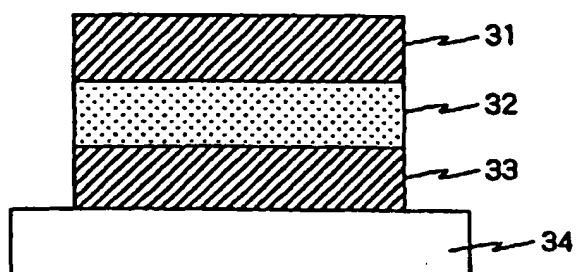


FIG. 4

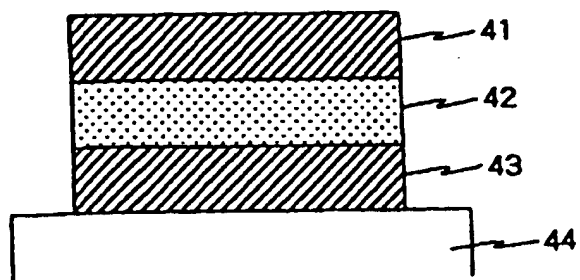


FIG. 5

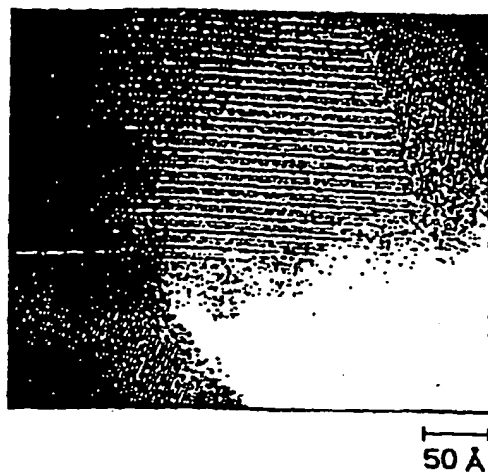


FIG. 6

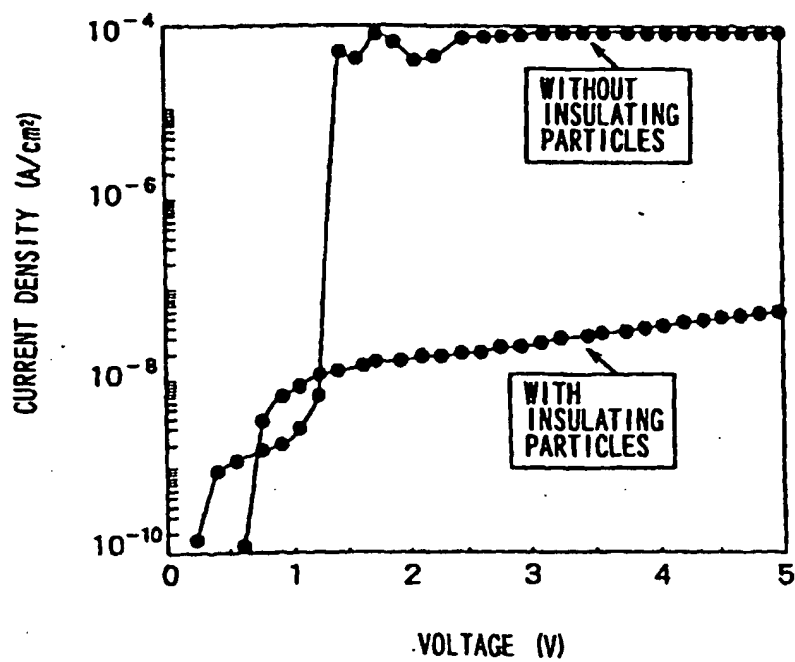


FIG. 7

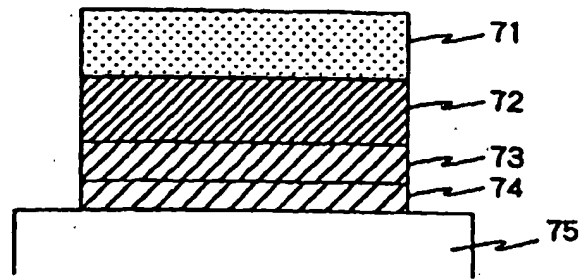


FIG. 8

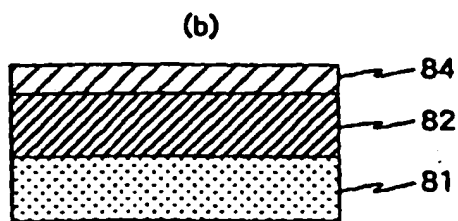
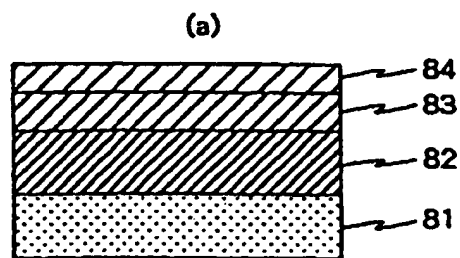


FIG. 9

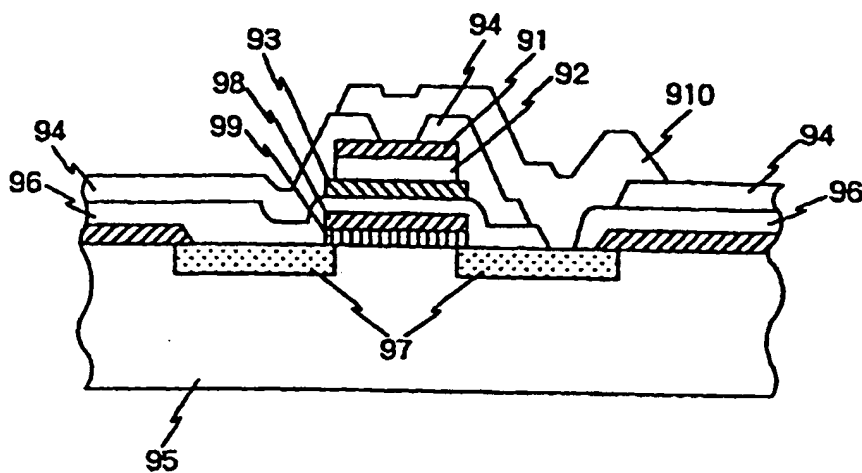
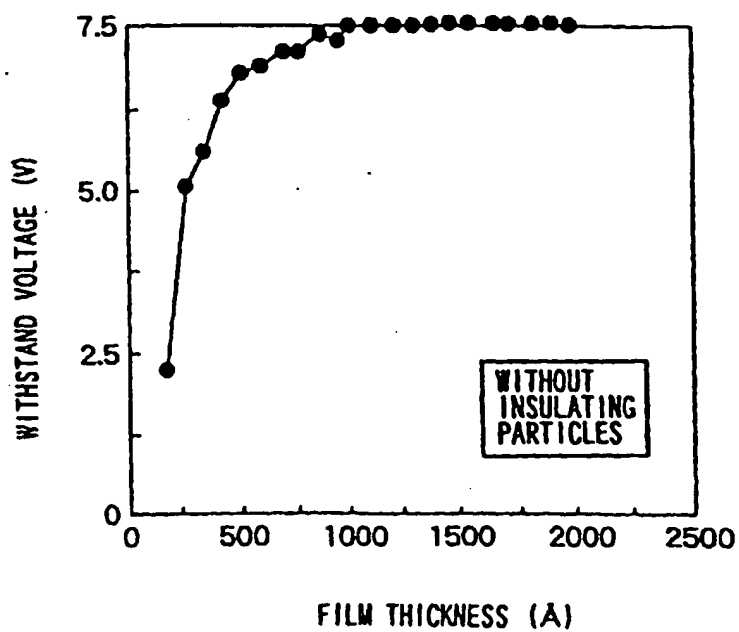


FIG. 10



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP97/04085

A. CLASSIFICATION OF SUBJECT MATTER Int.Cl. ¹ H01L21/3205, H01L21/8242, H01L27/10, H01L27/108, H01L27/115, H01L29/94, H01B3/12, H01G4/10, H01G4/12, H01G4/20, C03C10/02; According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) Int.Cl. ¹ H01L21/3205, H01L21/8242, H01L27/10, H01L27/108, H01L27/115, H01L29/94, H01B3/12, H01G4/10, H01G4/12, H01G4/20, C03C10/02, Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Jitsuyo Shinan Koho 1922-1997 Toroku Jitsuyo Shinan Koho 1994-1997 Kokai Jitsuyo Shinan Koho 1971-1997 Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) PAJ, WPI, EPOS, INSPEC, TDB, APS		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP, 8-31951, A (Texas Instruments Inc.), February 2, 1996 (02. 02. 96), Column 8, lines 12 to 41 ; Figs. 1, 2, 14, 15 (Family: none)	1-6, 9, 10 7, 8, 11-13, 19
X	JP, 9-36309, A (Matsushita Electronics Industry Corp.), January 15, 1997 (15. 01. 97), Claims 1 to 7 ; Fig. 1 & EP, 753887, A & KR, 97008668, A	1-6, 9, 10 7, 8, 11-13, 19
X	JP, 57-167669, A (Fujitsu Ltd.), October 15, 1982 (15. 10. 82), Figs. 4, 5 (Family: none)	1, 2, 3, 6
X	JP, 7-183397, A (Sharp Corp.), May 17, 1995 (17. 05. 95), Column 4, lines 9 to 19 ; Fig. 13 & EP, 653794, A & US, 5548475, A	14 19
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" documents which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later documents published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "Z" document member of the same patent family		
Date of the actual completion of the international search June 8, 1998 (08. 06. 98)		Date of mailing of the international search report June 16, 1998 (16. 06. 98)
Name and mailing address of the ISA/ Japanese Patent Office Facsimile No.		Authorized officer Telephone No.

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP97/04085

C(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP, 6-275548, A (Osaka Gas Co., Ltd.), September 30, 1994 (30. 09. 94), Table 1 (Family: none)	15
X	JP, 7-252664, A (Texas Instruments Japan Ltd., Tri-Chemical Lab, Inc.),	16, 17
Y	September 27, 1995 (27. 09. 95), Figs. 1, 2 & EP, 674019, A & TW, 298670, A	18
Y	JP, 6-283433, A (Olympus Optical Co., Ltd. Symetrix Corp.), October 7, 1994 (07. 10. 94), Column 13, lines 1 to 11 (Family: none)	18
Y	JP, 9-191087, A (NEC Corp.), July 22, 1997 (22. 07. 97), Figs. 1, 2 (Family: none)	7, 8, 11, 12, 13
X	JP, 4-170354, A (Murata Mfg. Co., Ltd.), June 18, 1992 (18. 06. 92), Fig. 1 (Family: none)	1, 6
Y	JP, 8-340086, A (Sharp Corp.), December 24, 1996 (24. 12. 96), Abstract (Family: none)	1, 2, 6
Y	US, 5555486, A (North Carolina State University), September 10, 1996 (10. 09. 96),	7-8
A	Claims 39-44, Fig. 1b & WO, 9621249, A & AU, 4608196, A	11-12
X	US, 5491102, A (Ceram Inc., Sharp, & Virginia Polytechnic),	7-8
A	February 13, 1996 (13. 02. 96), Column 4, lines 41 to 46 ; Claims & WO, 9321637, A & EP, 636271, A & JP, 6-68529, A	15-17
X	JP, 8-8403, A (Sharp Corp.), January 12, 1996 (12. 01. 96), Abstract (Family: none)	14
Y	JP, 3-19372, A (Seiko Epson Corp.),	1-2, 6
A	January 28, 1991 (28. 01. 91) (Family: none)	19
Y	JP, 63-301410, A (Murata Mfg. Co., Ltd.), December 8, 1988 (08. 12. 88) (Family: none)	1, 2, 4, 5, 6
Y	JP, 7-122681, A (Kyocera Corp.), May 12, 1995 (12. 05. 95) (Family: none)	1, 2, 4, 5, 6
Y	JP, 8-298380, A (Kyocera Corp.), November 12, 1996 (12. 11. 96) (Family: none)	1, 2, 4, 5, 6

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP97/04085

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US, 5668694, A (TDK Corp.), September 16, 1997 (16. 09. 97) & WO, 9613046, A & JP, 8-124784, A & JP, 8-124785, A & EP, 739019, A & CN, 1137326, A	1, 2, 4, 5, 6
Y	US, 5576564, A (Sharp Corp.), November 19, 1996 (19. 11. 96) & EP, 661754, A & JP, 7-202295, A	7-11, 13
Y	US, 5541807, A (J.T. Evans, Jr & R.H. Womack), July 30, 1996 (30. 07. 96) (Family: none)	7-13
Y	US, 5519566, A (Ramtron International Corp.) May 21, 1996 (21. 05. 96) (Family: none)	7-11, 13
Y	US, 5519235, A (Bell Communications Research Inc.), May 21, 1996 (21. 05. 96) & WO, 9616447, A & AU, 9641083, A & TW, 283234, A & EP, 792524, A	7-11, 13
Y	US, 5338951, A (Ramtron International Corp.), August 16, 1994 (16. 08. 94) & EP, 540994, A & JP, 5-218303, A	7-12
Y	US, 5471364, A (Texas Instruments Inc.), November 28, 1995 (28. 11. 95) & EP, 618598, A & JP, 6-350029, A	7-11, 13
Y	US, 5519234, A (Symetrix Corp.), May 21, 1996 (21. 05. 96) & WO, 9312542, A & AU, 9332738, A & EP, 616726, A	7-11, 13

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP97/04085

A. (Continuation) CLASSIFICATION OF SUBJECT MATTER

C04B35/47, C04B35/475, B32B18/00

B. (Continuation) FIELDS SEARCHED

C04B35/47, C04B35/475, B32B18/00